

EPA Stormwater Monitoring and Research Effort Summary

Mystic River Science Forum

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Overview

- Region 1 applied for and received Regional Applied Research Effort (RARE) and Regional Methods (RM) ORD grants to develop bacterial source tracking “Stormwater Toolbox”
- Sampling conducted throughout eastern New England with emphasis on Mystic River Watershed
- Minimum Recommended Screening Methods
- Mystic Watershed Summary

Project Goals

- Identify most effective and cost-efficient screening parameters; and
- Delineate and examine areas of possible illicit discharges; and
- Sampling coordination and collaboration within watershed.

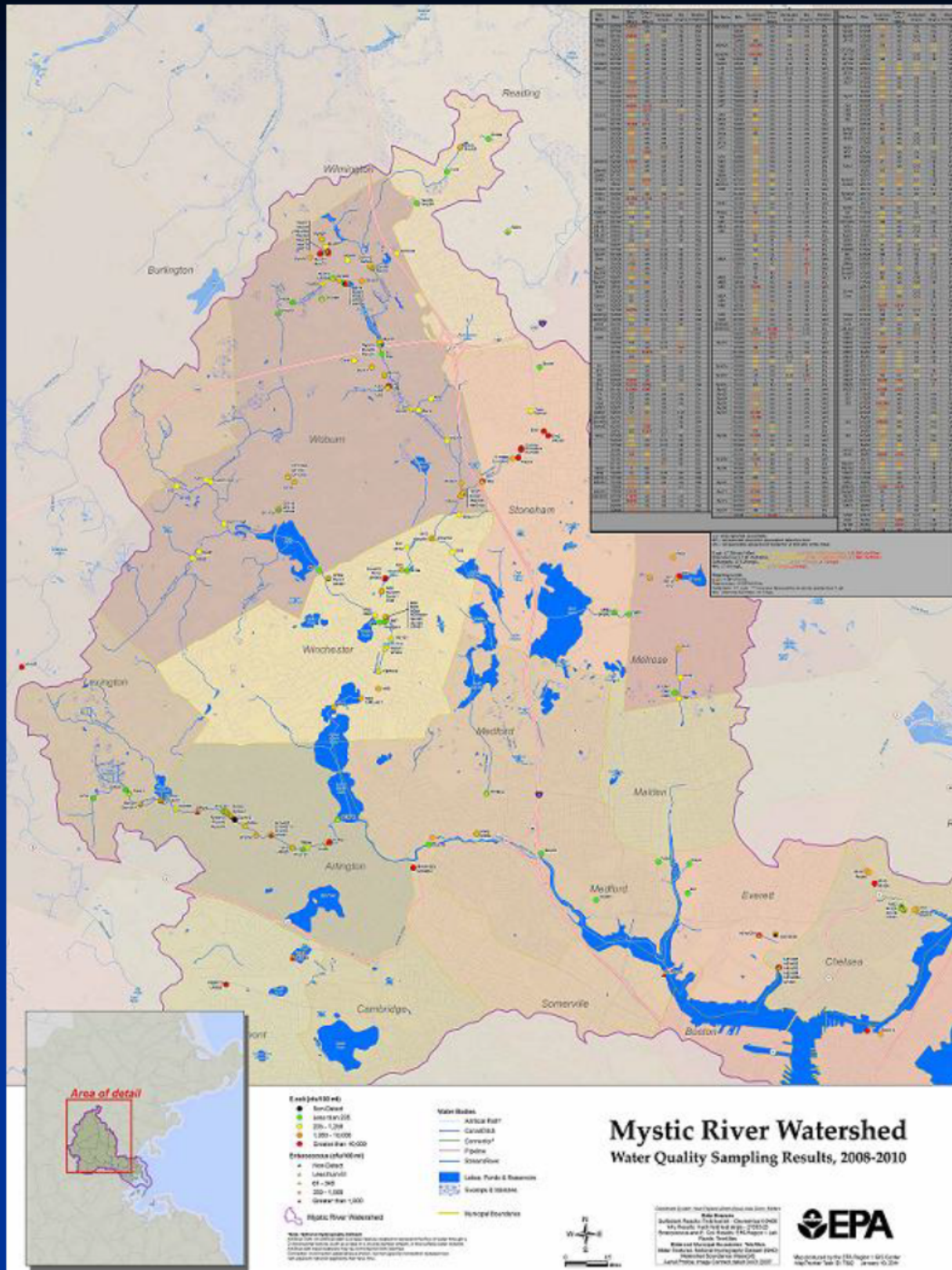
RARE/RM 2009 - 2010

Stormwater Sampling

2009 – 2010 Season:

- 335 sample sets were collected at 253 locations
- 1,110 laboratory samples
- 1,542 field kits or bench-top methods.
- Over 1,000 instrument readings
- Totaling over 3,657 water quality data points

Sample Location Overview



Map Created by:
EPA Region 1 GIS Dept.

Analytes tested for...

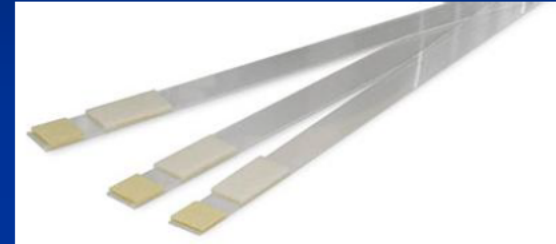
- ***E. coli**
- ***Enterococcus**
- ***Ammonia**
 - Alpha Analytical lab
 - Benchtop (DR-850 Hach)
 - Test kit – Hach (2 types)
 - Test strips
- ***Surfactants**
 - Alpha Analytical lab
 - Benchtop (DR-850 Hach)
 - Test kit – Chemetrics
- **Potassium**
- **Free and Total Chlorine**
 - Alpha Analytical lab
 - Test kit – Hach
 - Test strips
- **Total Phosphorus**
- **Fluoride**
 - Alpha Analytical lab
 - Benchtop (DR-850 Hach)
- **Pharmaceuticals**
 - Atenolol
 - Acetaminophen
 - Cotinine
 - 1,7-Dimethylxanthine
 - Caffeine
 - Azithromycin
 - Primidone
 - Urobilin
 - Carbamazepine
 - Sulfamethazine
 - Sulfamethoxazole
- **Urine test strips**

Recommended Minimum Screening Tests



Bacteria test

E. coli or
Enterococcus



Ammonia test strips



Surfactant test kit



Chlorine (total) test kit

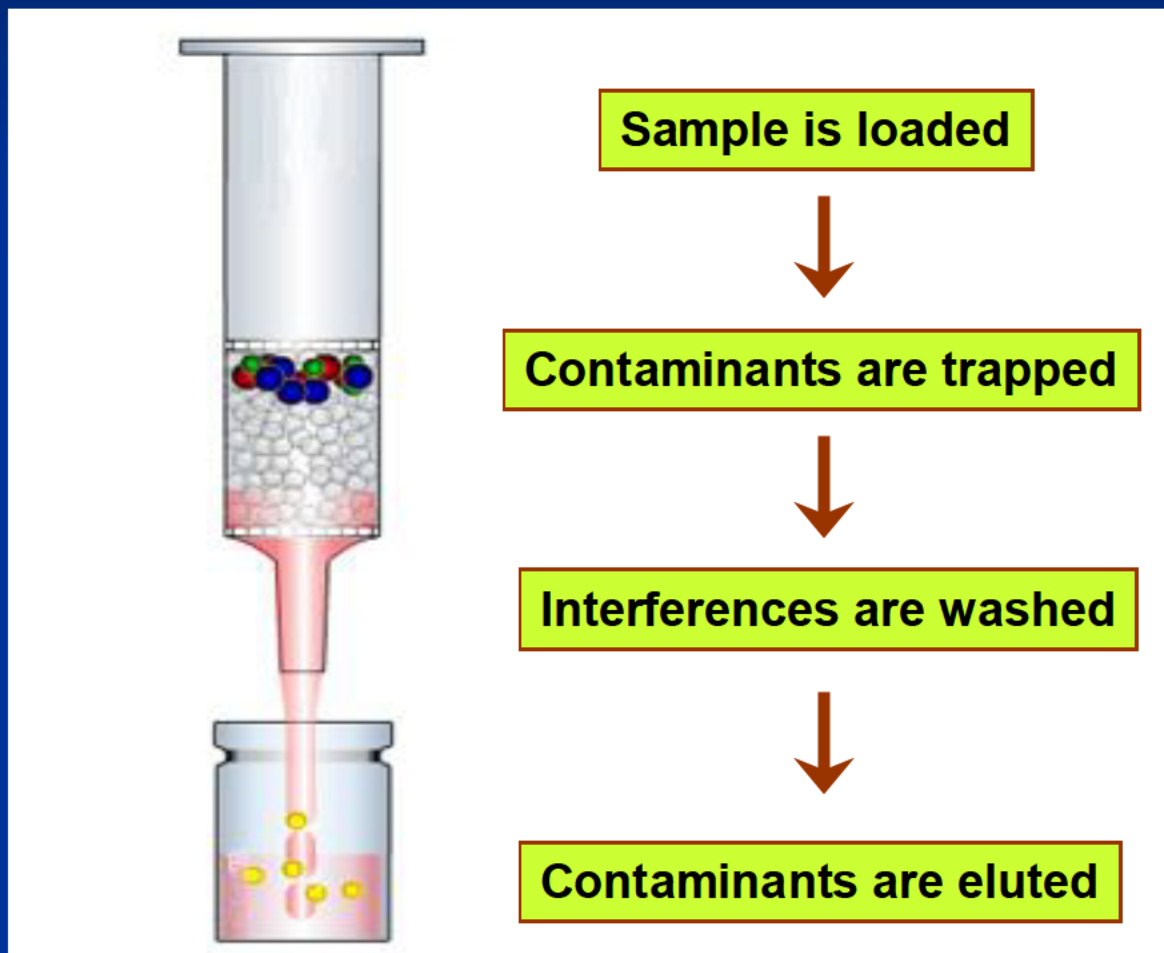
Target Compounds, Uses, and Reporting Limits

Target Compound	Major Use	RL (ng/L)	Daily Dose (ng)
Caffeine	Natural Stimulant	5.0	200,000,000
1,7-DMX	Metabolite of caffeine	2.5	N/A
Acetaminophen	Pain Reliever	2.5	650,000,000
Carbamazepine	Anti- depressant / bi-polar Anti-convulsant (epilepsy)	0.5	100,000,000
Primidone	Anti- epilepsy drug (AED)	5.0	100,000,000
Atenolol	Beta Blocker High Blood Pressure	2.5	50,000,000
Cotinine	Metabolite of Nicotine	0.5	3,500-7,200 (ng/mL)
Urobilin	By-product of hemoglobin breakdown (mammals)	5.0	1,300,000 ng/g in feces
Azithromycin	Antibiotic	1.6	200,000,000

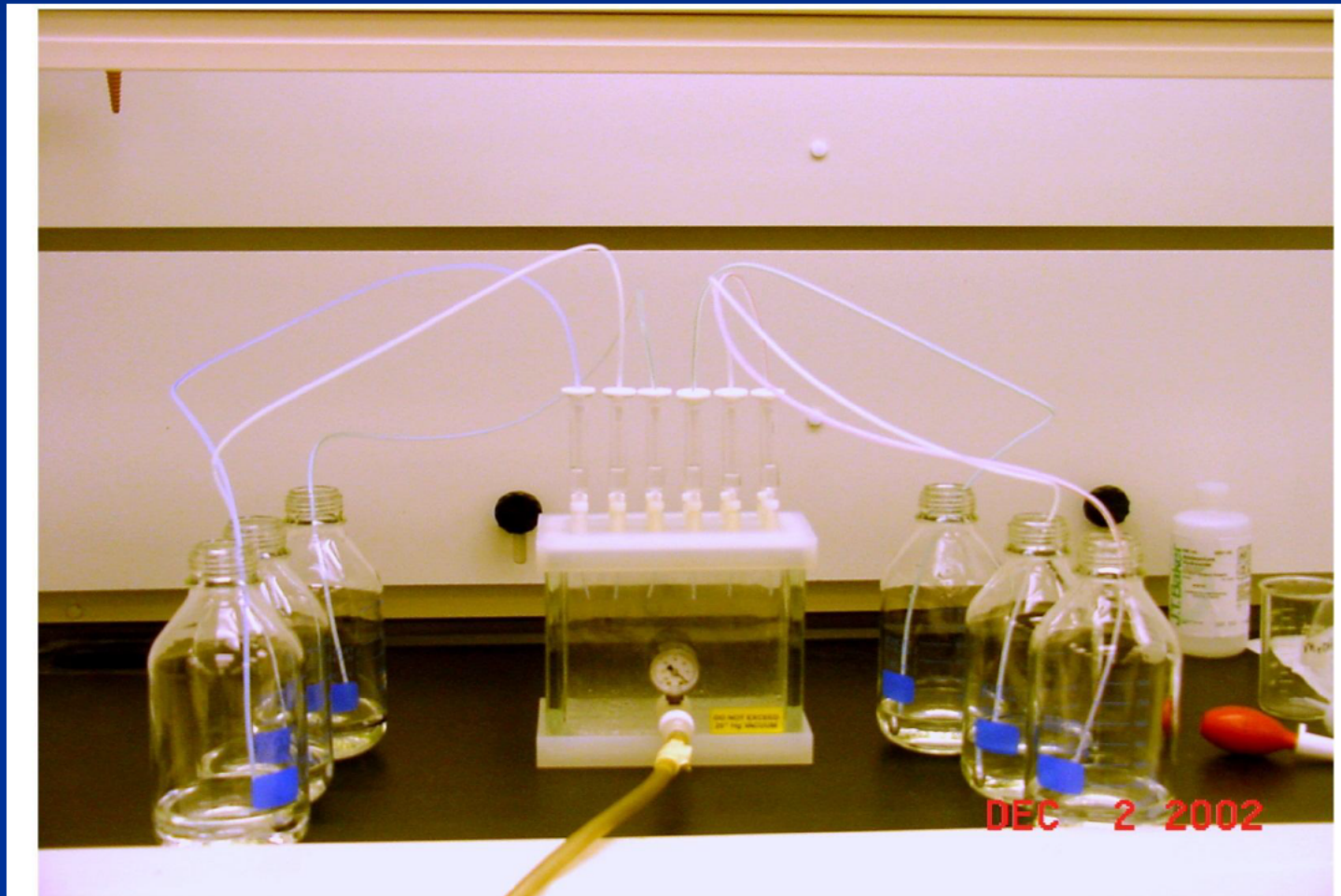
Sample Prep and SPE

- Samples are filtered
- Extracted within 7 days of collection
- Waters Oasis HLB Cartridge
- 500 mL sample
- Elution 1 with 100% MeOH
- Elution 2 with 99% MeOH 1% Acetic acid
- Extracts are concentrated to 1mL

Solid Phase Extraction (SPE)



Solid Phase Extraction Manifold



Synthesized Internal and Surrogate Standards

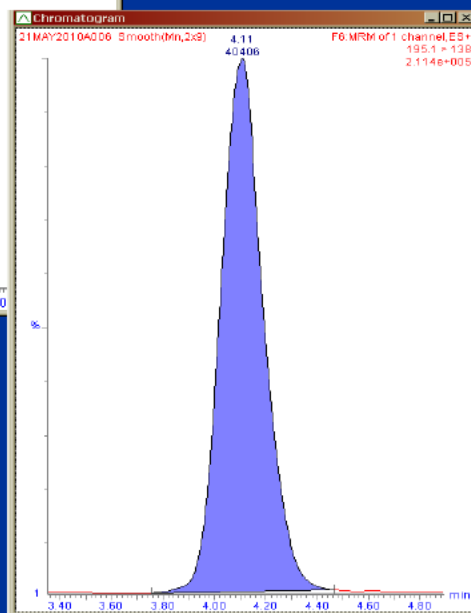
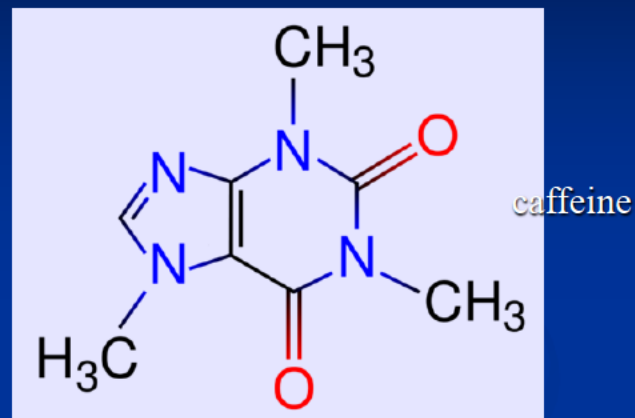
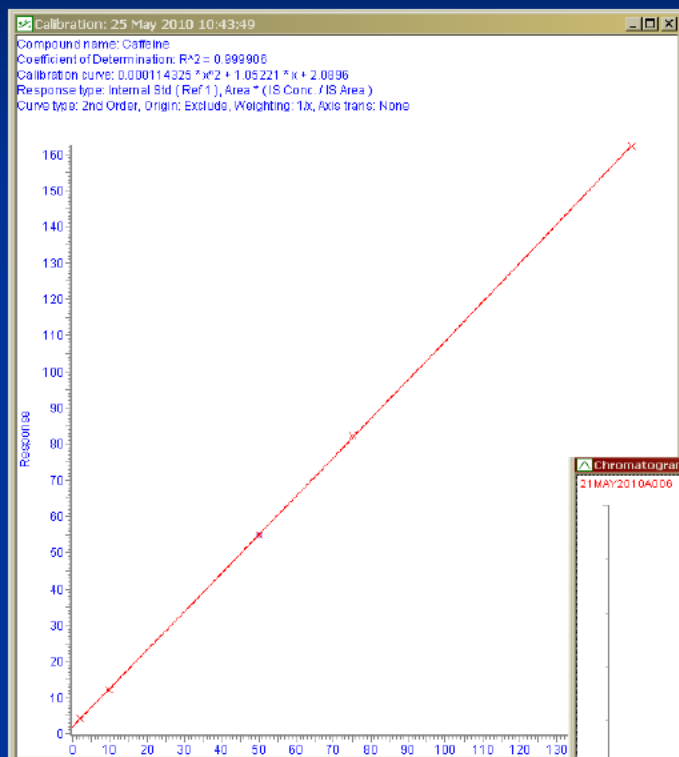
Caffeine 13C3	Surrogate Compound
Primidone d5	Surrogate Compound
Cotinine d3	Internal Standard
Carbamazepine d10	Internal Standard

Instrumental Analysis

- Chromatographic Separation by HPLC
- Simple Methanol / Water Gradient
- Electrospray Ionization (ESI) Positive
- Detection by Tandem Quadrupole Mass Spectrometry (MS/MS)



Calibration Curve and Quantitation



Compound	Conc. (ng/L)
1,7-Dimethylxanthine	1,800
Acetaminophen	8,800
Atenolol	920
Azithromycin	34
Caffeine	12,000
Carbamazepine	ND
Cotinine	86
Urobilin	79,000
Primidone	ND

Why Not Test All Samples?

- Time Intensive: It Takes ~ 20 Hours to Process each Batch of Samples (8 Field Samples)
- Instrumentation – The HPLC/MS/MS instrument costs $\sim \$500\text{K}$
- Solvent, Filtration, Hazardous Waste Disposal, SPE Cartridges Costs Exceed \$50 per Sample.
- Deuterated/ Isotopically Labeled Standards \$\$\$
- Very Few Labs Do This Analysis

Spot Pond Brook, Stoneham, MA



Analyte	Result
E. coli (MPN)	21
Surfactants	ND
Ammonia	ND
Caffeine	9.9 ng/L
1,7-Dimethylxanthine	7 ng/L
Urobilin	ND (2.0 ng/L)
Cotinine	ND (0.2 ng/L)
Acetaminophen	ND (1.0 ng/L)
Carbamazepine	ND (0.2 ng/L)
Atenolol	ND (2.0 ng/L)
Azithromycin	ND (2.0 ng/L)
Primidone	ND (2.0 ng/L)

Ryder Mill – Arlington, MA



Analyte	Result
E. coli (MPN)	1,302
Surfactants	0.3 mg/L
Ammonia	3.0 mg/L
Caffeine	520 ng/L
1,7-Dimethylxanthine	170 ng/L
Urobilin	15,000 ng/L
Cotinine	3.3 ng/L
Acetaminophen	15,000 ng/L
Carbamazepine	ND (0.5 ng/L)
Atenolol	250 ng/L
Azithromycin	67 ng/L
Primidone	ND (5.0 ng/L)

“Mill2a” - Chelsea Creek – Chelsea, MA



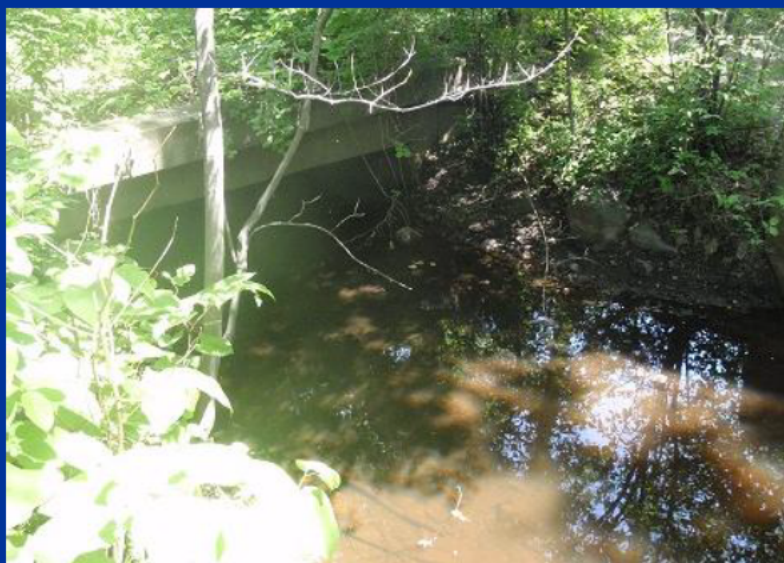
Analyte	Result
E. coli (MPN)	100
Surfactants	1 mg/L
Ammonia	6 mg/L
Caffeine	1,600 ng/L
1,7-Dimethylxanthine	67 ng/L
Urobilin	1,100 ng/L
Cotinine	46 ng/L
Acetaminophen	21 ng/L
Carbamazepine	9.8 ng/L
Atenolol	1.8 ng/L
Azithromycin	ND (2.0 ng/L)
Primidone	ND (2.0 ng/L)

Meetinghouse Brook, Medford, MA



Analyte	Result (Upstream)	Result (Downstream)
E. coli (MPN)	48	534
Surfactants	ND	0.1 mg/L
Ammonia	0.1 mg/L	ND
Caffeine	15 ng/L	33 ng/L
1,7-Dimethylxanthine	ND (2.0 ng/L)	21 ng/L
Urobilin	ND (4.0 ng/L)	230 ng/L
Cotinine	ND (0.4 ng/L)	ND (0.4 ng/L)
Acetaminophen	ND (2.0 ng/L)	170 ng/L
Carbamazepine	ND (0.4 ng/L)	6.0 ng/L
Atenolol	ND (2.0 ng/L)	6.9 ng/L
Azithromycin	ND (0.4 ng/L)	2.1 ng/L
Primidone	ND (4.0 ng/L)	ND (4.0 ng/L)

Mill Brook, Arlington, MA



Analyte	Result (Upstream)	Result (Downstream)
E. coli (MPN)	16	2,318
Surfactants	ND	ND
Ammonia	ND	0.75
Caffeine	5.8 ng/L	98 ng/L
1,7-Dimethylxanthine	ND (2.5 ng/L)	19 ng/L
Urobilin	390 ng/L	2,700 ng/L
Cotinine	1.5 ng/L	12 ng/L
Acetaminophen	2.6 ng/L	23 ng/L
Carbamazepine	ND (0.5 ng/L)	1.9 ng/L
Atenolol	ND (2.5 ng/L)	32 ng/L
Azithromycin	ND (0.5 ng/L)	0.84 ng/L
Primidone	ND (5.0 ng/L)	ND (4.0 ng/L)

Future Watershed Work

- MWRA 205/City of Somerville
- Arlington outfalls to Mill Brook
- Stoneham common manholes; illicit; chronic SSO
- Halls Brook (Woburn)
- Salem Street (Woburn)
- Mill Brook (Arlington/Lexington line)
- Winns Brook (Belmont)
- Wellington Brook (Belmont)
- City of Revere Judicial Consent Decree
- Boston Water and Sewer Commission outfalls

RARE/RM Next Steps

- Complete data review, summary, recommendations
- Continued enforcement
- Bacteria, surfactant, ammonia, chlorine
- Volunteer monitoring equipment loan program
- Will post results, maps and related information on EPA Region 1 website for Mystic River, which can be found at:
www.epa.gov/mysticriver

Questions?